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Radiolytic Studies of the Mechanism of Autoxidation of Triphenylphosphine and Related Compounds

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Triphenylphosphine (Ph_3P) undergoes one-electron oxidation in irradiated CH_2Cl_2 solutions to yield the radical cation $Ph_3P^{\bullet+}$. This short-lived species exhibits intense absorption with a maximum at 325 nm and an extended shoulder at 400−500 nm and decays by a second-order process in the absence of O_2. In the presence of O_2, however, the radical cation reacts with O_2 with a rate constant of 7×10^6 L mol^{-1} s^{-1} to yield a peroxyl radical, $Ph_3P^+OO^\bullet$, which exhibits no significant absorbance at $\lambda > 300$ nm. Similar results, but with slightly different rate constants, were obtained also in CCl_4 solutions and in CH_3CN and cyclohexane solutions containing 1% CCl_4. Tris(2,4,6-trimethoxyphenyl)phosphine in CH_2Cl_2 exhibits a behavior similar to that of Ph_3P, but the reaction of its radical cation with O_2 is an order of magnitude more rapid. On the other hand, the perfluorinated $Ph_3P^{\bullet+}$ in CH_2Cl_2 reacts with O_2 much more slowly, if at all. Diphenyl-2-pyridylphosphine yields a radical cation which exhibits a slightly narrower absorption band but reacts with O_2 with the same rate constant as $Ph_3P^{\bullet+}$. The peroxyl radicals propagate a chain reaction by further oxidation of phosphine molecules to $Ph_3P^{\bullet+}$ either directly or indirectly. The final radiolysis product is the phosphine oxide, Ph_3PO. The radiolytic yields for oxidation of the phosphines were much higher than the radiolytic yield of the solvent derived radicals, except for the case of the perfluoro derivative, and were dependent on the concentrations of phosphine and O_2 and on the dose rate. At low dose rates and high solute concentrations the chain lengths exceeded 1000.

Introduction

Triphenylphosphine is one of several compounds being evaluated as potential additives for enhancing the stability of future jet fuels toward thermal oxidation.[1] It has been recently demonstrated to improve the thermal oxidative stability of one jet fuel by at least 50%. The mechanism of its action as an oxygen-removing agent was suggested[1] to involve initial formation of the radical cation of triphenylphosphine, reaction of the radical cation with O_2 to form a peroxyl radical, and chain propagation via reaction of this peroxyl radical with another molecule of Ph_3P. The present study is aimed at elucidating the mechanism of autoxidation of Ph_3P by using radiolytic methods to initiate the oxidation, to observe transient species, and to determine the kinetics of the reactions involved.

Irradiation of triphenylphosphine on the surface of porous glass was suggested[2] to lead to formation of the radical cation, which exhibits optical absorption peaks at 330, 345, and 438 nm. Irradiation of CCl_4 glassy solutions at 77 K also indicated formation of $Ph_3P^{\bullet+}$, but the spectrum was reported to have a broad peak around 530 nm and was not measured at $\lambda < 400$ nm.[3] Pulse radiolysis permitted the observation of this transient species in solution; its spectrum in chlorocyclohexane was found to have a broad absorption around 500 nm and increasing absorption at $\lambda < 420$ nm, but the measurements were not continued for $\lambda < 400$ nm.[4] No kinetic details were given in the previous articles. In the present study we examine the oxidation of Ph_3P in CH_2Cl_2, CCl_4, CH_3CN, and cyclohexane solutions both by pulse radiolysis to follow the formation and reactions of the radical cation and by γ-radiolysis to study the presumed chain reaction, and we compare the behavior of several phosphine derivatives.

Experimental Section

Triphenylphosphine and its derivatives were obtained from Aldrich[5] and the solvents from Mallinckrodt. They were obtained in the highest available purity and were used as received. Solutions were prepared immediately before irradiation and were protected from light to prevent the UV photolytic oxidation of the phosphines by O_2. γ-radiolysis experiments were carried out mostly under air in a Gammacell 220 ^{60}Co source with a dose rate of 0.79 Gy s^{-1}. A number of experiments were carried out in deoxygenated (Ar-purged) and in O_2-saturated solutions and also in another ^{60}Co source with a dose rate variable between 0.029 and 0.0066 Gy s^{-1}. The radiolytic yield of oxidation of the triphenylphosphines to the corresponding phosphine oxides was determined from the changes in absorbance following irradiation with various doses.

The observation of transient species and the determination of their kinetic behavior were performed with the NIST pulse radiolysis apparatus. Solutions were irradiated with a 50 ns pulse of 2 MeV electrons, and the formation and decay of transient species were followed by kinetic spectrophotometry at various wavelengths. The dose per pulse was generally between 5 and 50 Gy. There are two major sources of uncertainty in the derived rate constants: the statistical uncertainties in the first-order fits of the kinetic traces and in the plots of k_{obs} vs concentration, which were generally between 5

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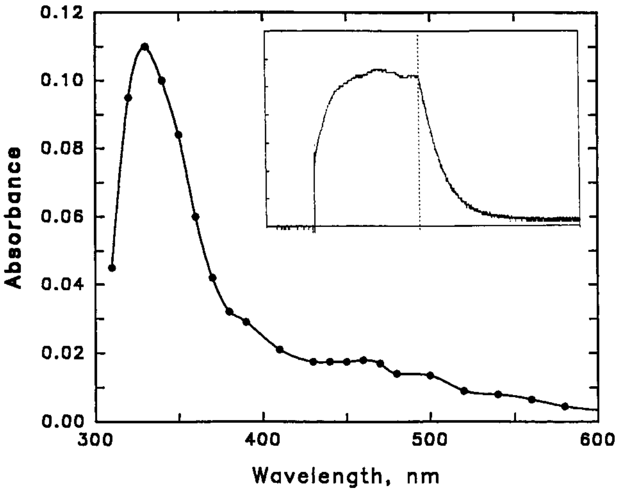

Figure 1. Optical absorption spectrum of triphenylphosphine radical cation. Recorded by pulse radiolysis of CH_2Cl_2 solutions containing 1×10^{-3} mol L^{-1} Ph_3P under air, 10 μs after the pulse. The insert shows a plot of absorbance at 330 nm vs time: 20 μs for the left half and 300 μs overall for the right half.

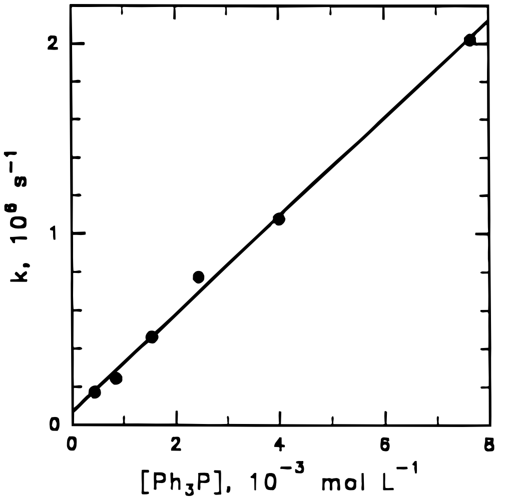

Figure 2. First-order rate constant for formation of $Ph_3P^{\bullet+}$, monitored by growth of absorbance at 340 nm, as a function of triphenylphosphine concentration, in aerated CH_2Cl_2 solutions.

and 10%, and uncertainties in the measurements of volumes, weights, and in the concentration of O_2, which we estimate as ≤10%. The overall estimated standard uncertainties are given along with the rate constants. Other details of the apparatus were given before.[6] All experiments were performed at room temperature, 20 ± 2 °C.

Results and Discussion

Radiolysis of many organic compounds in CH_2Cl_2 and in CCl_4 solutions has been shown to lead to the production of one-electron-oxidized species.[6,7] Oxidation may occur in several steps. The strongly oxidizing species formed upon radiolysis of these solvents, mainly solvent radical cations and chlorine atoms, are relatively short-lived (in the nanosecond range or less) and thus react with solutes only when these are present at sufficiently high concentrations to scavenge these species before they decay. In addition, peroxyl radicals are formed in these solvents under air. These radicals are weaker oxidants and longer-lived than the Cl atoms and solvent radical cations, but they may oxidize certain solutes, albeit more slowly.

To produce the radical cations of the various triphenylphosphines, we irradiated CH_2Cl_2 and CCl_4 solutions of these compounds. Kinetic spectrophotometric pulse radiolysis experiments with 1 mmol L^{-1} Ph_3P solutions under air showed the formation of absorbance in the UV and visible range. The spectrum recorded 10 μs after the pulse exhibits a strong peak at 330 nm (with molar absorptivity of about 6×10^3 L moL^{-1} cm^{-1})[8] and a substantial shoulder at 400−500 nm (Figure 1) and is ascribed to the radical cation, $Ph_3P^{\bullet+}$. This spectrum is in agreement with earlier results; the main peak and the shoulder are in agreement with those obtained in irradiated glass,[2] and the shoulder was also reported in a pulse radiolytic study in solution,[4] where the spectrum at $\lambda > 420$ nm was recorded. The absorbance was formed in two steps; a substantial fraction was seen immediately after the pulse (within <0.1 μs), due to rapid oxidation of Ph_3P by the short-lived solvent radical cations and chlorine atoms, and the rest was formed by gradual buildup over about 10 μs, due to the slower oxidation by the peroxyl radicals (Figure 1, insert). From the dependence of the absorbance growth rate on $[Ph_3P]$ (Figure 2), the rate constant for the latter process was found to be $(2.6 \pm 0.5) \times 10^8$ L mol^{-1} s^{-1} in CH_2Cl_2 and $(8.6 \pm 1.5) \times 10^8$ L mol^{-1} s^{-1} in CCl_4. These rate constants are ascribed to reactions 1 and 2, respectively.

$$Ph_3P + CHCl_2OO^{\bullet} \rightarrow Ph_3P^{\bullet+} + CHCl_2OO^{-} \qquad (1)$$

$$Ph_3P + CCl_3OO^{\bullet} \rightarrow Ph_3P^{\bullet+} + CCl_3OO^{-} \qquad (2)$$

When the solutions were bubbled with Ar, to remove O_2 and prevent the formation of the peroxyl radicals, the immediate formation step was observed but the slower step practically vanished.

In the absence of O_2 the decay of $Ph_3P^{\bullet+}$ followed a second-order rate law, indicating the occurrence of radical−radical reactions ($2k$ is estimated to be 3×10^9 L mol^{-1} s^{-1}). The decay of $Ph_3P^{\bullet+}$ in air-saturated solutions followed almost pure first-order rate law and was about 10 times more rapid than in the absence of O_2, indicating reaction of $Ph_3P^{\bullet+}$ with O_2. The rate constant for this process in air-saturated solutions was 2.5×10^4 s^{-1}. When the solution was saturated with pure O_2 instead of air, the decay of $Ph_3P^{\bullet+}$ was much faster, and the rate constant observed was 8.7×10^4 s^{-1}. From these two rate constants, and the solubility of O_2 in CH_2Cl_2 (0.0107 mol L^{-1} under 1 atm of O_2),[9] the second-order rate constant for the reaction of $Ph_3P^{\bullet+}$ with O_2 was calculated to be $(7.3 \pm 1.4) \times 10^6$ L mol^{-1} s^{-1}. Similar experiments with CCl_4 solutions gave a rate constant of $(2.0 \pm 0.4) \times 10^7$ L mol^{-1} s^{-1}. We ascribe these rate constants to reaction 3.

$$Ph_3P^{\bullet+} + O_2 \rightarrow Ph_3P^{+}OO^{\bullet} \qquad (3)$$

The values of k_3 are about 100−400 times slower than those for the reactions of carbon-centered radicals with O_2[10] and are more in line with the behavior expected of nitrogen-centered radicals.[11] In addition, the low rate constants for reaction 3 are reasonable in view of the fact that most radical cations have not been found to react with O_2. Actually, it is somewhat surprising to find a radical cation reacting with O_2 at such a measurable rate.

Three other phosphines were examined in CH_2Cl_2 solutions. Diphenyl-2-pyridylphosphine was oxidized slightly more slowly, $k_1 = (1.8 \pm 0.3) \times 10^8$ L mol^{-1} s^{-1}, possibly due to electron withdrawing by the pyridyl group which lowers the electron density on P. On the other hand, the reaction of the radical cation with O_2 took place with the same rate constant as that for $Ph_3P^{\bullet+}$, $k_3 = (7.7 \pm 1.4) \times 10^6$ L mol^{-1} s^{-1}. The spectrum of the radical cation also was similar to that of $Ph_3P^{\bullet+}$; the main peak was slightly narrower and more intense, but the main peak position and the extended shoulder were similar. Tris(2,4,6-trimethoxyphenyl)phosphine was oxidized more rapidly due to electron donating by the methoxyl groups and also possibly due to stabilization of the radical cation via mesomeric forms with the positive charge on the oxygen, as polymethoxybenzenes are known to give relatively stable radical cations.[12] The spectrum of the radical cation was similar to that of $Ph_3P^{\bullet+}$ except that the main peak was slightly broader and less intense. The reaction of $[(MeO)_3Ph]_3P^{\bullet+}$ with O_2 was also more rapid, $k_3 = (1.5 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1}. This is in line with the mesomeric effect of the *ortho* and *para* methoxyl groups, which increases the electron density on the phosphorus, and also with the through-space overlap of the 2p electrons on the *ortho* methoxyl oxygen with the vacant 3d orbital of the P, which may have an even stronger effect.[13] In contrast, the perfluorinated triphenylphosphine underwent much slower oxidation to produce a similar radical cation, and this species reacted with O_2, if at all, too slowly to be measured on the pulse radiolysis time scale; i.e., the reaction with O_2 did not compete with the second-order decay of the radical cations.

Radiolytic oxidation of Ph_3P was also achieved in acetonitrile solutions under air. A rate constant of $(9 \pm 2) \times 10^8$ L mol^{-1} s^{-1} was determined for the oxidation step. The dependence of the first-order rate on $[Ph_3P]$ was linear but with a large intercept, 1.5×10^6 s^{-1}, indicating that the oxidizing species is much shorter lived than the other peroxyl radicals. This suggests that the oxidation is not by the peroxyl radical $CNCH_2OO^\bullet$, whose lifetime is in the millisecond range,[14] but rather by an oxidizing precursor such as the solvent radical cation.[15] When 1% CCl_4 was added to the acetonitrile solutions to scavenge the electrons, oxidation by the resulting $CCl_3OO^\bullet$ radicals was observed, with a rate constant similar to that in neat CCl_4 solutions. The rate of reaction of the radical cation with O_2 in acetonitrile was close to those found in the other solvents, $k_3 = (1.0 \pm 0.2) \times 10^7$ L mol^{-1} s^{-1}.

To use a solvent that is closer in character to fuels, we carried out radiolytic oxidation of Ph_3P also in cyclohexane solutions containing 1% CCl_4. This additive forms $CCl_3OO^\bullet$ radicals, which oxidize the phosphine, but the yield of $Ph_3P^{\bullet+}$ was considerably lower than that found in neat CCl_4 or CH_2Cl_2, because the yield of free electrons in cyclohexane is lower. $Ph_3P^{\bullet+}$ in cyclohexane reacted with O_2 with $k_3 = (2.4 \pm 0.5) \times 10^7$ L mol^{-1} s^{-1}, almost 3 times faster than in CH_2Cl_2. In argon-purged solutions the absorption was weaker and decayed more slowly by a second-order process.

Radiolysis of Ph_3P in methanol solutions did not lead to formation of the radical cation. This indicates that Ph_3P is not oxidized by the $HOCH_2OO^\bullet$ peroxyl radicals sufficiently rapidly to compete with their radical–radical decay. Moreover, oxidation by the $CH_3O^\bullet$ radical, which is known to be produced in irradiated methanol and to oxidize several compounds,[16] did not take place, indicating that the reaction was too slow (with $[Ph_3P] < 0.01$ mol L^{-1}) to compete with the rapid decay of the methoxyl radical. Furthermore, addition of methanol to the Ph_3P solutions in CH_2Cl_2 and CCl_4 decreased the yield of oxidation dramatically. This is due to rapid scavenging of the positive ions and Cl atoms by methanol to produce a weak oxidant.

The above rate constants for reaction 3 were measured by following the decay of $Ph_3P^{\bullet+}$ at various $[O_2]$ but at constant $[Ph_3P]$. However, when the rate of decay of $Ph_3P^{\bullet+}$ was measured over a wide range of $[Ph_3P]$, from 4×10^{-4} mol L^{-1} to 7×10^{-2} mol L^{-1}, the rate constant in air-saturated CH_2Cl_2 solutions was found to depend on $[Ph_3P]$. At low concentrations, between 4×10^{-4} and 4×10^{-3} mol L^{-1}, it was constant at about 2.5×10^4 s^{-1}, but when $[Ph_3P]$ was increased to 2.3×10^{-2} and 5.5×10^{-2} mol L^{-1}, the rate of decay became clearly slower; it decreased to 1.6×10^4 and 0.8×10^4 s^{-1}, respectively. Moreover, at $[Ph_3P] \geq 5.5 \times 10^{-2}$ mol L^{-1}, the decay did not fit a first-order but rather a second-order rate law. These results suggest that at high concentrations of Ph_3P a mechanism exists for re-forming $Ph_3P^{\bullet+}$ and thus making its decay appear slower and second order; i.e., this suggests a chain reaction.

One possible mechanism is that the peroxyl radical formed by reaction 3 oxidizes another molecule of Ph_3P directly.

$$Ph_3P^+OO^\bullet + Ph_3P \rightarrow Ph_3P^+OO^- + Ph_3P^{\bullet+} \qquad (4)$$

This reaction may be feasible, since Ph_3P can be oxidized by chlorinated alkylperoxyl radicals, although not by hydroxymethylperoxyl, and since it is known that peroxyl radicals containing an ammonium or a phenyl group at the α-carbon are more reactive than alkylperoxyl.[17] In fact, the phosphonium group, being attached directly to the peroxyl group, should have a strong enhancing effect on the reactivity of this peroxyl as an oxidant. Another possible mechanism is oxidation by oxygen atom transfer via the following two steps.

$$Ph_3P^+OO^\bullet + Ph_3P \rightarrow Ph_3P^+O^\bullet + Ph_3PO \qquad (5)$$

$$Ph_3P^+O^\bullet + Ph_3P \rightarrow Ph_3PO + Ph_3P^{\bullet+} \qquad (6)$$

Reaction 5 is similar in mechanism to that suggested for reactions of some peroxyl radicals with phosphines[18] (and with some sulfides[19] and tellurides[20]). The products are phosphine oxide, which is the stable product observed in the γ-radiolysis experiments described below, and a phosphinoxyl radical. The latter radical is expected to be a stronger oxidant than $Ph_3P^+OO^\bullet$ (as most oxyl radicals are stronger oxidants than the corresponding peroxyl) and should readily oxidize Ph_3P via reaction 6 to produce another radical cation. Although both of the above alternative mechanisms appear to be feasible, and although it is possible that both mechanisms operate in parallel, as found for the sulfides,[19] the mechanism via reactions 5 and 6 produces the final product that is known to be formed whereas reaction 4 yields the zwitterionic hydroperoxide, $Ph_3P^+OO^-$, which has to undergo further steps to form the final products.

If we assume that at high $[Ph_3P]$ most of the $Ph_3P^{\bullet+}$ disappearing in reaction 3 is recovered via reaction 4 or reactions 5 and 6, i.e., that the overall rates of these steps are similar at about 0.1 mol L^{-1} Ph_3P, we can estimate the rate constant for reaction 4 or 5 (or their sum) to be about 2×10^5 L mol^{-1} s^{-1}. This is a very rough estimate, based on the assumption that $[O_2]$ is the same in all solutions studied. However, if $[O_2]$ was lower at the higher Ph_3P concentrations, due to partial autoxidation of the phosphine, which depletes more O_2 at high $[Ph_3P]$ than at low $[Ph_3P]$, then the above estimate is only an upper limit. Another approach to estimate the contribution of reactions 4 and 5 is by examining the chain reaction at low dose rates in γ-radiolysis experiments.

To confirm that the oxidized phosphine species engage in a chain process, we examined the overall radiolytic yield of the oxidation of Ph_3P in CH_2Cl_2 solutions. This was accomplished by measuring changes in optical absorbance of the solutions as a function of irradiation dose. The UV spectrum of Ph_3P has a broad peak at 260 nm (with a molar absorptivity of about 9×10^3 L mol^{-1} cm^{-1} and a width at half-height of ~50 nm). When the solution was irradiated in a ^{60}Co source (or by a strong UV light), this broad peak gradually decreased in intensity and was replaced with a weak spectrum that has three sharp peaks

TABLE 1: Radiolytic Yields for Oxidation of Triarylphosphines

medium	dose rate (Gy s^{-1})	[Ar$_3$P] (mmol L^{-1})	G^a (μmol J^{-1})	G_{initial} (μmol J^{-1})
I. Triphenylphosphine				
CH_2Cl_2, air	~0.4^b	5.75	137	145
		2.87	111	122
		1.37	81	95
		0.69	46	56
		0.34	29	38
		0.17	18	25
		0.09	11	17
	0.0285	2.74	370	400
		1.37	340	380
		0.68	201	231
		0.34	117	139
	0.0066	2.74	840	903
		1.37	596	642
		0.68	408	465
		0.34	257	305
CH_2Cl_2, Ar		9.51	1.0	
		0.42	0.2	
CH_2Cl_2+4% MeOH, air	~0.4	5.14	78	81
CCl_4, air		1.97	52	54
CCl_4, Ar		1.97	0.7	
CH_3CN, air		2.37	18	19
CH_3CN, Ar		2.37	0.03	
c-C_6H_{12}, air		1.53	4.9	5.0
c-C_6H_{12}+0.2% CCl_4, air		0.71	6.0	7.1
II. Diphenyl-2-pyridylphosphine				
CH_2Cl_2, air		1.85	220	340
CH_2Cl_2, Ar		1.85	0.95	
III. Tris(2,4,6-trimethoxyphenyl)phosphine				
CH_2Cl_2, air		2.31	270	390
IV. Tris(pentafluorophenyl)phosphine				
CH_2Cl_2, air		2.25	2.0	2.0

[a] The standard uncertainty for the experimental *G* values is estimated to be generally around 10%. [b] The nominal dose rate of the Gammacell used was 0.79 Gy s^{-1}. However, these short irradiations were done partly during the lowering and raising of the drawer and thus the dose rate was not constant. A rough estimate of the dose rate is the average between 0 and 0.79 and is taken as ~0.4 Gy s^{-1}.

at 260, 266, and 272 nm. These peaks were confirmed to be due to the product triphenylphosphine oxide by use of an authentic sample of this material. From the change in absorbance with irradiation time and the known dose rate, we calculate the radiation yield for the oxidation of Ph_3P. The results are summarized in Table 1. With solutions in which $[Ph_3P] > [O_2]$, the oxidation nearly stops after a certain irradiation dose, indicating that diffusion of oxygen into the solution from the air space above it is quite slow. However, when the solution is resatuarated with air, the chain oxidation continues upon further radiolysis.

The concentration of Ph_3P was found to decrease exponentially with irradiation time (Figure 3), i.e.

$$[Ph_3P] = [Ph_3P]_0 e^{-kt} \tag{7}$$

This equation permits us to calculate the initial radiolytic yields (*G*) even when the measurements were done after substantial decrease in concentration (which was unavoidable at low $[Ph_3P]$). The actual measurements provide the yield from the change in $[Ph_3P]$, the dose rate *I*, and the time of irradiation *t*, i.e., $G = ([Ph_3P]_0 - [Ph_3P])/It$. From eq 7, $[Ph_3P]_0 - [Ph_3P] = [Ph_3P]_0(1 - e^{-kt})$. For $kt << 1$, i.e., short irradiation times, $1 - e^{-kt} \simeq kt$, and thus

$$G = k[Ph_3P]_0/I \tag{8}$$

This is a more accurate way of deriving *G* values, since larger uncertainties are usually associated with measurements of small differences in $[Ph_3P]$ to obtain initial yields than with measurement of *k* from the change in $[Ph_3P]$ as a function of time. The *G* values calculated by this method are also given in Table 1 as G_{initial}.

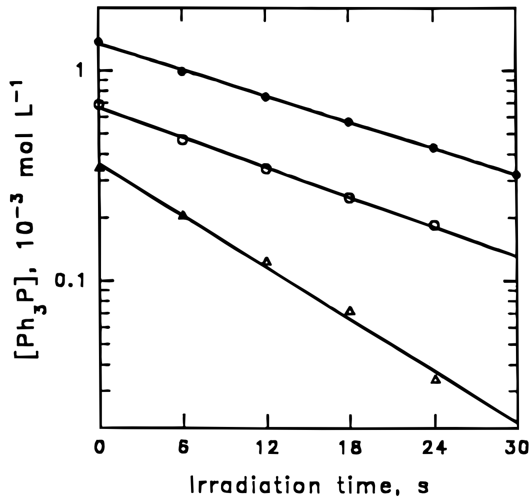

Figure 3. Exponential decrease in triphenylphosphine concentration as a function of irradiation time. Aerated CH_2Cl_2 solutions were irradiated in the Gammacell with an average dose rate of ~0.4 Gy s^{-1} (see footnote *a* in Table 1). The initial concentrations of Ph_3P were 1.37×10^{-3} (●), 6.9×10^{-4} (○), and 3.4×10^{-4} mol L^{-1} (△).

It is clearly seen from Table 1 that the *G* values for oxidation of Ph_3P in the presence of air are up to 3 orders of magnitude larger than the *G* values for the formation of oxidizing ions and radicals in CH_2Cl_2 (0.75 μmol J^{-1}),[6] indicating the involvement of a long chain reaction. The chain length, calculated as the ratio between $G(-Ph_3P)$ and the maximum *G* value of initial phosphine radical cations, reaches up to 1200. Since the *G* for oxidation of Ph_3P in Ar-saturated solutions is much lower and is similar to the yield of the initial solvent radicals, the chain in the presence of air must be due to Ph_3P^+-$OO^\bullet$. This peroxyl radical may propagate the chain by oxidizing a molecule of Ph_3P to its radical cation (reaction 4 or reactions 5 and 6). Termination can occur by combination or disproportionation of two radicals of any type.

Table 1 shows that the *G* values depend on the dose rate. The two lower dose rates give a clear dependence of *G* on $I^{1/2}$ as is commonly found in radiation-induced chain reactions.[21] The higher dose rate used is not a constant dose rate (see footnote *a* in Table 1), but if we use the arithmetic average of the dose rate, the relation with $I^{1/2}$ holds quite closely even over a change in dose rate by a factor of 60.

Table 1 also shows that the *G* value depends on $[Ph_3P]$. However, Figure 4 indicates that this dependence is not linear as is usually found in radiation-induced polymerization chain reactions.[21] Rather, a dependence close to $c^{1/2}$ is observed. This is due to the fact that in polymerization chain reactions all the radicals involved in the propagation and termination, whether the monomer $M^\bullet$ or a polymeric $M_n^\bullet$, independent of its chain length, have similar reactivities, whereas in the present system two different radicals are involved with clearly different reactivities. Furthermore, these different radicals are present in different proportions, depending on $[Ph_3P]$. For long chains with two propagation steps,[22] the steady-state assumption for the two radicals requires equal rates for the two reactions, i.e.

$$\text{rate of propagation} = k_3[Ph_3P^{\bullet+}][O_2] = k_4[Ph_3P^+OO^\bullet][Ph_3P] \tag{9}$$

leading to

$$[\mathrm{Ph_3P^{\bullet+}}]/[\mathrm{Ph_3P^+OO^\bullet}] = k_4[\mathrm{Ph_3P}]/k_3[\mathrm{O_2}] \qquad (10)$$

Since the initial concentration of $\mathrm{O_2}$ is the same in all experiments (air-saturated $\mathrm{CH_2Cl_2}$ containing 2.2×10^{-3} mol $\mathrm{L^{-1}}$ $\mathrm{O_2}$), the higher the $\mathrm{Ph_3P}$ concentration, the higher is the steady-state concentration of $\mathrm{Ph_3P^{\bullet+}}$, as the sum of $[\mathrm{Ph_3P^{\bullet+}}] + [\mathrm{Ph_3P^+OO^\bullet}]$ is constant and is determined by the rate of formation of $\mathrm{Ph_3P^{\bullet+}}$ by the radiation and the rate of termination of radicals. Let us examine two extreme cases, where termination occurs by one type of radical. If we assume that all terminations occur by reaction of two $\mathrm{Ph_3P^{\bullet+}}$ radical cations,

$$2\mathrm{Ph_3P^{\bullet+}} \rightarrow \text{products} \qquad (11)$$

The steady-state assumption for $\mathrm{Ph_3P^{\bullet+}}$ requires that the rate of termination will be equal to the rate of initiation, $k_i = k_{11}[\mathrm{Ph_3P^{\bullet+}}]^2$, i.e., $[\mathrm{Ph_3P^{\bullet+}}] = (k_i/k_{11})^{1/2}$. Substituting this into the equation for the rate of propagation leads to

$$\text{rate of propagation} = (k_i/k_{11})^{1/2}k_3[\mathrm{O_2}] \qquad (12)$$

As can be seen from this equation, the rate of propagation, equal to the *GI* values, is independent of $[\mathrm{Ph_3P}]$, as the concentration of $\mathrm{O_2}$ is the same for all air-saturated solutions. However, if we assume that all terminations occur through reaction of two peroxyl radicals

$$2\mathrm{Ph_3P^+OO^\bullet} \rightarrow \text{products} \qquad (13)$$

then $k_i = k_{13}[\mathrm{Ph_3P^+OO^\bullet}]^2$ and thus $[\mathrm{Ph_3P^+OO^\bullet}] = (k_i/k_{13})^{1/2}$, and the rate of propagation is given by

$$\text{rate of propagation} = (k_i/k_{13})^{1/2}k_4[\mathrm{Ph_3P}] \qquad (14)$$

In this case G is proportional to $[\mathrm{Ph_3P}]$. In the case of termination only by mixed radical reactions, $\mathrm{Ph_3P^{\bullet+}} + \mathrm{Ph_3P^+OO^\bullet}$, the rate of propagation is proportional to $[\mathrm{Ph_3P}]^{1/2}[\mathrm{O_2}]^{1/2}$. However, when all termination reactions occur simultaneously, G will depend on $[\mathrm{Ph_3P}]^\alpha$ with $0 < \alpha < 1$, and α may happen to be ~ 0.5. So from $\alpha \neq 0$ or $\alpha \neq 1$ no conclusion on the main termination step can be drawn, except to say that both radicals are involved in termination processes.

Another proof for the suggested mechanism is that if we derive the dependence of G on $[\mathrm{Ph_3P}]$ from one solution irradiated with various doses, then we find a linear dependence of G on $[\mathrm{Ph_3P}]$. Figure 3 shows that during the whole irradiation $[\mathrm{Ph_3P}] = [\mathrm{Ph_3P}]_0 e^{-kt}$, which leads to $[\mathrm{Ph_3P}]_{t2} = [\mathrm{Ph_3P}]_{t1} e^{-k(t2-t1)}$, and then we obtain, as in eq 8, that $G = k[\mathrm{Ph_3P}]_{t1}/I$. Since k is constant during the irradiation, G is linearly proportional to $[\mathrm{Ph_3P}]$. However, it should be pointed out that during the irradiation $[\mathrm{O_2}]$ also changes, while for solutions initially prepared with different concentrations of $\mathrm{Ph_3P}$ the initial $[\mathrm{O_2}]$ is the same. For both mechanisms, as *GI* is proportional to $k_i^{1/2}$ and as k_i, the rate of formation of radicals by the radiation, is proportional to I, G will depend on $I^{-1/2}$.

These equations can be correlated with the observed rate constants measured by pulse radiolysis. Assuming termination by $\mathrm{Ph_3P^{\bullet+}}$ alone, then $k_3[\mathrm{O_2}]$ was measured by pulse radiolysis to be 2.5×10^4 $\mathrm{s^{-1}}$, $k_i = 3 \times 10^{-7}$ L $\mathrm{mol^{-1}}$ $\mathrm{s^{-1}}$, $k_{11} = 3 \times 10^9$ L $\mathrm{mol^{-1}}$ $\mathrm{s^{-1}}$, and hence the rate of propagation is 2.9×10^{-4} $\mathrm{s^{-1}}$ as compared to 7.3×10^{-5} $\mathrm{s^{-1}}$ found in our experiments for 1×10^{-3} mol $\mathrm{L^{-1}}$ and 1.2×10^{-4} $\mathrm{s^{-1}}$ for 5.7×10^{-3} mol $\mathrm{L^{-1}}$. The difference may be due to the fact that the termination is not only by $\mathrm{Ph_3P^{\bullet+}}$.

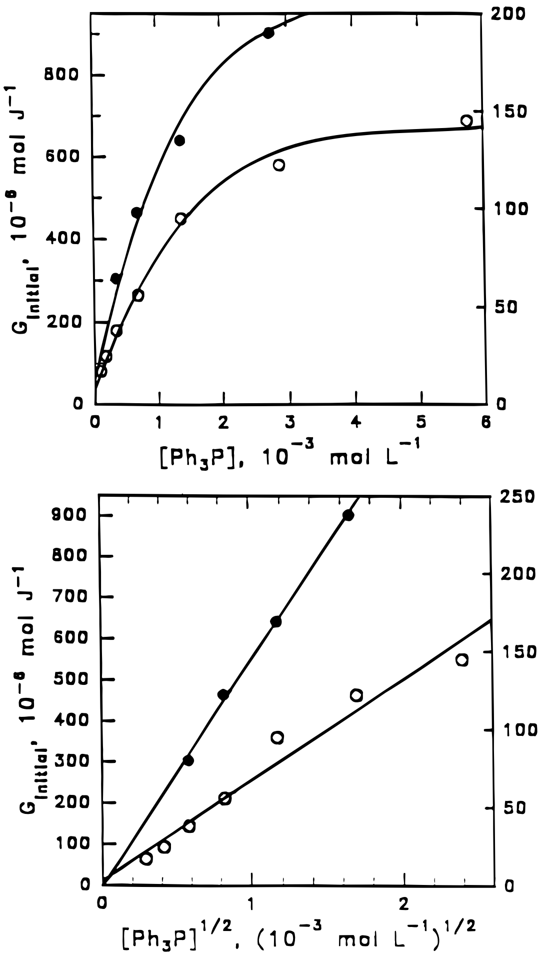

Figure 4. Dependence of the initial radiolytic oxidation yield of $\mathrm{Ph_3P}$ on the initial concentration of $\mathrm{Ph_3P}$ in air-saturated $\mathrm{CH_2Cl_2}$ solutions. Both linear and square root dependences are shown. (●) Left vertical scale, 0.0066 Gy $\mathrm{s^{-1}}$; (○) right vertical scale, ~0.4 Gy $\mathrm{s^{-1}}$.

Although 4% MeOH added to $\mathrm{CH_2Cl_2}$ solutions reduced the absorbance of $\mathrm{Ph_3P^{\bullet+}}$ in the pulse radiolysis by a factor of 4−5, the G value for disappearance of $\mathrm{Ph_3P}$ in the γ-radiolysis is reduced only by a factor of about 2, indicating that while methanol interferes with the initial formation of $\mathrm{Ph_3P^{\bullet+}}$, it does not interfere with the chain process. It should be remembered that change of initiation by a factor of 4 should reduce the G value only by a factor of 2, as the rate of propagation is proportional to $k_i^{1/2}$.

The chain is shorter in $\mathrm{CCl_4}$ than in $\mathrm{CH_2Cl_2}$ and even shorter in acetonitrile. This is probably due to the effect of the solvent on the rate constants for reactions 4−6, as the rate constant for reaction 3 was changed only by a small factor and in the opposite direction. A much shorter chain was found in cyclohexane, but small concentrations of $\mathrm{CCl_4}$ increased the chain yield due to larger rate of initiation (by $\mathrm{CCl_3OO^\bullet}$).

Longer chains were found for $\mathrm{PyPh_2P}$ and $[\mathrm{(MeO)_3Ph}]_3\mathrm{P}$. In the latter case this can be attributed at least partly to the higher rate constant for reaction of the radical cation with $\mathrm{O_2}$, as determined by pulse radiolysis. In the case of $\mathrm{PyPh_2P}$, the pulse radiolysis shows a lower rate constant for the formation of the radical cation, which suggests that the longer chain is due to higher rate constants for the propagation reactions parallel to reactions 4 and 5, i.e., that $\mathrm{Ph_2PyP^+OO^\bullet}$ is more reactive than the triphenyl analogue. In contrast with these two compounds, and in accordance with the nonreactivity of $\mathrm{(F_5Ph)_3P}$ with $\mathrm{O_2}$ found in the pulse radiolysis, a very short chain was found for oxidation of this derivative in $\mathrm{CH_2Cl_2}$ solutions.

For comparison with the above findings with triphenylphosphine, we carried out several experiments with triphenylamine. First, triphenylphosphine is found to be oxidized relatively rapidly by several peroxyl radicals whereas triphenylamine was not.[23] Second, γ-radiolysis of CH_2Cl_2 solutions of Ph_3N under air indicated disappearance of the amine with a radiolytic yield of only 0.17 μmol J^{-1}, i.e., less than half the yield of the initial oxidizing species (0.75 μmol J^{-1}), and no chain reaction. Third, the radical cation of triphenylamine did not react with O_2 in the pulse radiolysis experiment. Pulse radiolysis of Ph_3N in CH_2Cl_2 produced the radical cation, $Ph_3N^{\bullet+}$, which has an optical absorption peak at 640 nm as observed before.[4] This absorbance was relatively long-lived at low amine concentrations but decayed at higher concentrations to produce another species. From this decay we estimate an upper limit for the rate constant of the reaction of $Ph_3N^{\bullet+}$ with O_2 of $<5 \times 10^6$ L mol^{-1} s^{-1}.[24] The above three differences in the behavior of triphenylamine as compared with triphenylphosphine enable the latter compound, but not the former, to enhance the thermal oxidative stability of fuels.

The finding that $Ph_3N^{\bullet+}$ exhibits a strong absorbance with a maximum at 640 nm whereas $Ph_3P^{\bullet+}$ exhibits a peak at 320 nm and only a shoulder at 400−500 nm is related to the difference in the structures of these two radical cations. $Ph_3N^{\bullet+}$ attains a flattened structure, and thus the unpaired spin is delocalized on the rings; this provides the lower energy transitions observed. On the other hand, although oxidation of Ph_3P to $Ph_3P^{\bullet+}$ results in considerable flattening of the molecule, the latter radical cation retains an equilibrium geometry that is still pyramidal.[25] In this geometry, about 85% of the unpaired spin is localized on the P atom.[26] This minimal delocalization results in the absorption band being at a higher energy than that for $Ph_3N^{\bullet+}$. Furthermore, the localized triphenylphosphine radical cations can form dimers with P−P bonding whereas the delocalized triphenylamine radical cations dimerize through C−C bonding mainly in their *para* positions.

The results presented above provide kinetic and mechanistic information to explain why triarylphosphines, but not triarylamines, might serve as additives for enhancing the stability of future jet fuels toward thermal oxidation. The results further indicate how changes in the arylphosphine structure influence the rate constants for the reaction of the arylphosphine radical cation with O_2 and the reaction of the resulting peroxyl radical with another phosphine molecule, i.e., in the rates of the chain propagation steps. Continuation of our study of the effect of phosphine structure on these rate constants may facilitate the design of a phosphine structure for optimal fuel stabilization.

References and Notes

(1) Beaver, B. D.; De Munshi, R.; Sharief, V.; Tian, D.; Teng, Y. 5th Int. Conf. Stability Handling Liq. Fuels, Rotterdam, the Netherlands, 1995; pp 241−254. Also see: Beaver, B. D.; De Munshi, R.; Heneghan, S. P.; Whitacre, S. D.; Neta, P. *Energy Fuels*, in press.

(2) Wong, P. K.; Allen, A. O. *J. Phys. Chem.* **1970**, *74*, 774.

(3) Shida, T.; Hamill, W. H. *J. Chem. Phys.* **1966**, *44*, 2369.

(4) Burrows, H. D.; Greatorex, D.; Kemp, T. J. *J. Phys. Chem.* **1972**, *76*, 20.

(5) The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

(6) Alfassi, Z. B.; Mosseri, S.; Neta, P. *J. Phys. Chem.* **1989**, *93*, 1380.

(7) Grodkowski, J.; Neta, P. *J. Phys. Chem.* **1984**, *88*, 1205 and references therein.

(8) The molar absorptivity was estimated from experiments at higher concentrations, where full scavenging of the oxidizing radicals is achieved, and taking oxidation yield in CH_2Cl_2 as 0.75 μmol J^{-1}, ref 6.

(9) Murow, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; p 290.

(10) Neta, P.; Grodkowski, J.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1996**, *25*, 709. Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1990**, *19*, 413.

(11) Vieira, A. J. C. S.; Steenken, S. *J. Am Chem. Soc.* **1987**, *109*, 7441.

(12) O'Neill, P.; Schulte-Frohlinde, D.; Steenken, S. *Faraday Discuss. Chem. Soc.* **1977**, *63*, 141 and references therein.

(13) McEwen, W. E.; Lau, K. W. *J. Org. Chem.* **1982**, *47*, 3595. Keldsen, G. L.; McEwen, W. E. *J. Am. Chem. Soc.* **1978**, *100*, 7312.

(14) Mosseri, S.; Neta, P.; Meisel, D. *Radiat. Phys. Chem.* **1990**, *36*, 683.

(15) Baptista, J. L.; Burrows, H. D. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 2066.

(16) Dainton, F. S.; Janovsky, I. V.; Salmon, G. A. *J. Chem. Soc., Chem. Commun.* **1969**, 335. Ellison, D. H.; Salmon, G. A.; Wilkinson, F. *Proc. R. Soc. London A* **1972**, *328*, 23.

(17) Neta, P.; Huie, R. E.; Mosseri, S.; Shastri, L. V.; Mittal, J. P.; Maruthamuthu, P.; Steenken, S. *J. Phys. Chem.* **1989**, *93*, 4099.

(18) Furimski, E.; Howard, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 369.

(19) Schöneich, C.; Aced, A.; Asmus, K.-D. *J. Am. Chem. Soc.* **1991**, *113*, 375.

(20) Engman, L.; Persson, J.; Merenyi, G.; Lind, J. *Organometallics* **1995**, *14*, 3641.

(21) Spinks, J. W. T.; Woods, R. J. *Introduction to Radiation Chemistry*, 3rd ed.; Wiley: New York, 1990; pp 186−190.

(22) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Wiley: New York, 1995; pp 73−76.

(23) Shoute, L. C. T.; Neta, P. *J. Phys. Chem.* **1990**, *94*, 2447.

(24) The secondary product formed upon decay of the initial radical cation exhibits a very broad absorption with a maximum at 820−850 nm, as observed by Sumiyoshi: Sumiyoshi, T. *Chem. Lett.* **1995**, 645. The rate of formation of this secondary product was dependent on $[Ph_3N]$, and the process was ascribed to a reaction of $Ph_3N^{\bullet+}$ with another molecule of Ph_3N. In our experiments, the first-order rate constant of the decay of $Ph_3N^{\bullet+}$ was also found to be linearly dependent on $[Ph_3N]$, with an intercept of 1×10^4 s^{-1}. This intercept is due to self-reactions of the radical cations and their reactions with impurities in the solvent and with O_2. If we ascribe the intercept totally to their reaction with O_2, we derive an upper limit for the rate constant of this reaction of $k < 5 \times 10^6$ L mol^{-1} s^{-1}. Further studies are underway to clarify this system, but the upper limit for this rate constant is valid independently of the mechanism involved.

(25) Tordo, P. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: New York, 1990; Vol. 1, Chapter 6, p 137.

(26) Berclaz, T.; Geoffroy, M. *Mol. Phys.* **1975**, *30*, 549.